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Klarskov, Mikkel Buster; Dam, Henrik Friis; Petersen, Dirch Hjorth; Hansen, Torben Michael; Löwenborg, A; Booth, Tim; Schmidt, Michael Stenbæk; Lin, R; Nielsen, P F; Bøggild, Peter

Published in:
Nanotechnology

Link to article, DOI:
[10.1088/0957-4484/22/44/445702](https://doi.org/10.1088/0957-4484/22/44/445702)

Publication date:
2011

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Klarskov, M. B., Dam, H. F., Petersen, D. H., Hansen, T. M., Löwenborg, A., Booth, T., Schmidt, M. S., Lin, R., Nielsen, P. F., & Bøggild, P. (2011). Fast and direct measurements of the electrical properties of graphene using micro four-point probes. *Nanotechnology*, 22(44), 445702. <https://doi.org/10.1088/0957-4484/22/44/445702>

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2011 Nanotechnology 22 445702

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Fast and direct measurements of the electrical properties of graphene using micro four-point probes

M B Klarskov¹, H F Dam¹, D H Petersen¹, T M Hansen¹,
A Löwenborg¹, T J Booth¹, M S Schmidt¹, R Lin², P F Nielsen² and
P Bøggild¹

¹ Department of Micro- and Nanotechnology, Technical University of Denmark,
DTU Nanotech, Building 345E, DK-2800 Kongens Lyngby, Denmark

² CAPRES A/S, Scion-DTU, Building 373, DK-2800 Kongens Lyngby, Denmark

E-mail: mikkel.olesen@nanotech.dtu.dk

Received 8 July 2011, in final form 14 September 2011

Published 6 October 2011

Online at stacks.iop.org/Nano/22/445702

Abstract

We present measurements of the electronic properties of graphene using a repositionable micro four-point probe system, which we show here to have unique advantages over measurements made on lithographically defined devices; namely speed, simplicity and lack of a need to pattern graphene. Measurements are performed in ambient, vacuum and controlled environmental conditions using an environmental scanning electron microscope (SEM). The results are comparable to previous results for microcleaved graphene on silicon dioxide (SiO₂). We observe a pronounced hysteresis of the charge neutrality point, dependent on the sweep rate of the gate voltage; and environmental measurements provide insight into the sensor application prospects of graphene. The method offers a fast, local and non-destructive technique for electronic measurements on graphene, which can be positioned freely on a graphene flake.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since the first demonstration of isolated graphene and its field effect properties [1], much effort has been focused on its electrical properties [2], since the carriers in graphene behave as massless fermions with a linear dispersion relation around the Dirac points [3].

The typical approach toward testing the electrical properties of graphene is by patterning the graphene into a suitable geometry and depositing electrodes by photo- or electron beam (e-beam) lithography [1, 4, 5]. In the case of microcleaved graphene, the lithography pattern must be aligned to the individual graphene flake, followed by at least one round of exposure, development, metallization and lift-off. Large-area graphene from chemical vapor deposition (CVD) and epitaxial growth on silicon carbide is less restrictive in terms of alignment, but still requires definition of a field effect transistor-like electrode geometry [6].

With the drastic increase in available graphene area [7, 8], the verification of the electronic properties of as-produced graphene becomes increasingly important, and will constitute a quickly narrowing bottleneck for industrial development and research. Furthermore, the lithographic patterning of graphene leads to irreversible changes to the sample, and previous results show that the lithography process itself may change the electronic properties, leaving resist residues, contaminants etc [9, 10].

An obvious solution is to use repositionable electrodes. Several scanning probe techniques have been applied to the characterization of graphene, such as scanning probe gate measurement of the charge neutrality point [11], and electrostatic force microscopy [12]. Conducting atomic force microscopy (AFM) is also possible [13]; however, here it was demonstrated that the bias voltage can lead to undesirable patterning of the graphene through local anodic oxidation [13]. Although these methods probe the

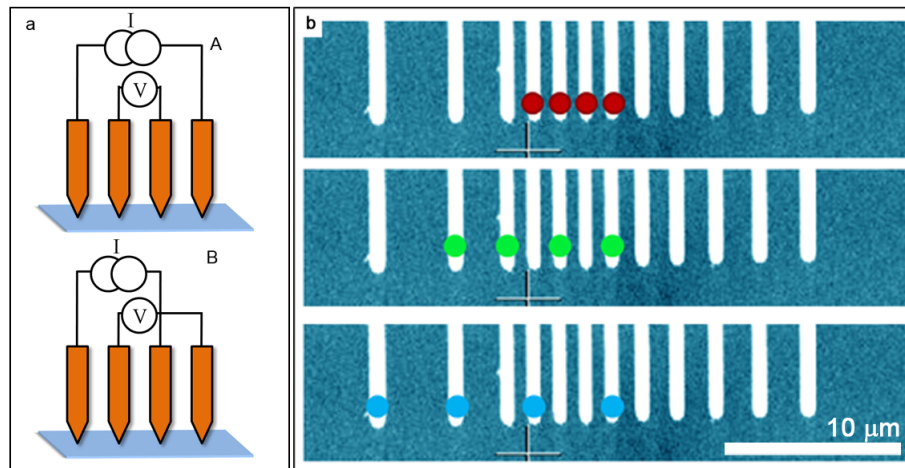


Figure 1. (a) Illustration of M4PP with two different measurement configurations, A and B, where V measures the voltage drop, and I indicates a current source. (b) Optical image of the 12-point probe used in ambient measurements. Three different pitches are indicated, 1.5 μm , 3.0 μm and 4.5 μm , respectively.

electrical properties, lithographic definition of at least one electrode on the graphene sample is still required. Recently, four independently positioned electrodes were applied for rotational square configuration measurements of multi-layer epitaxial graphene on SiC in a $100 \times 100 \mu\text{m}^2$ measurement area [14]. Although this technique allows for anisotropic conductance characterization [15], microfabricated four-point probes (M4PP) [16] are much simpler to operate, and do not involve individual alignment of the scanning probe tips. This makes mapping a practical possibility, which has been demonstrated for numerous other materials including conjugated monolayer polymers [17] and non-uniform ultra-thin semiconductors with lateral dimensions down to $10 \times 10 \mu\text{m}^2$ [18]. In addition, it has recently been shown that the Hall carrier mobility and carrier density can be extracted from collinear four-point probe measurements [19]. Multiple previous measurements of the conductance of graphene using lithographically defined fixed electrodes have been made, falling in the range 0.1–8 mS [20–22], and the conductivity of graphene particles has been measured at 64 mS cm^{-1} using standard four-point probe techniques [23].

In this work we show that repositionable, monolithic micro four-point probes provide a fast, local and non-destructive technique for measuring the electrical properties of graphene, despite the extreme thinness of the material and the mechanical contact required. We show that the method can be used in both ambient and vacuum conditions, and employ environmental scanning electron microscopy (ESEM) to investigate the effect of the local environment.

2. Methods

The current investigation involves equidistant M4PP measurements on micromechanically cleaved graphene samples. Two electrodes are used for sourcing a current, I , and the other two for measuring the corresponding voltage drop, V . Two different measurement modes were used; single and dual configuration. In the single configuration mode we calculate

the sheet conductance $\sigma = I/(cV)$, where c is the geometrical correction factor [24]. Due to position errors of the electrodes there is a unique static error on the geometrical correction factor. Using dual configuration, this static position error is eliminated [25], as well as geometrical errors caused by finite sample size [27]. Figure 1(a) illustrates the two current/voltage electrode configurations used for dual configuration position correction, A and B.

Graphene samples were produced by mechanical exfoliation of graphite on low-resistivity wafers with thermally grown 90 nm silicon dioxide (SiO_2) film. Prior to the exfoliation, the wafers were baked at 120°C and cleaned in O_2/N_2 plasma for 5 min. Gate voltage was controlled by a back-side contact; however, to improve M4PP to surface alignment, top-side connections were preferred. To avoid chemical interaction with the graphene, the top electrode was made by removing an area of the SiO_2 by reactive ion etching and metal deposition using a shadow mask.

3. Ambient conditions

The measurements in ambient conditions (i.e. in air at room temperature and pressure) were obtained using a commercial Capres MicroRSP-M150 system with Capres M12PP probes (see figure 1(b)), from which the equidistant pitch configurations 1.5, 3 and 4.5 μm were selected for the measurements. An AC current of 1 μA was used. The time for making a measurement was 5 min, with a gate voltage sweep from 0 V to +60 V and back to 0 V.

Figure 2 displays a typical dual configuration measurement of the conductance as a function of applied gate voltage in ambient conditions. Three different pitches were used, indicated by the three different curves, and two different measurement configurations were combined [25, 26] to give the result shown. Defining hysteresis as the difference in the conductance minima, we observe a pronounced hysteresis of approximately 35 V. Such hysteresis effects are commonplace

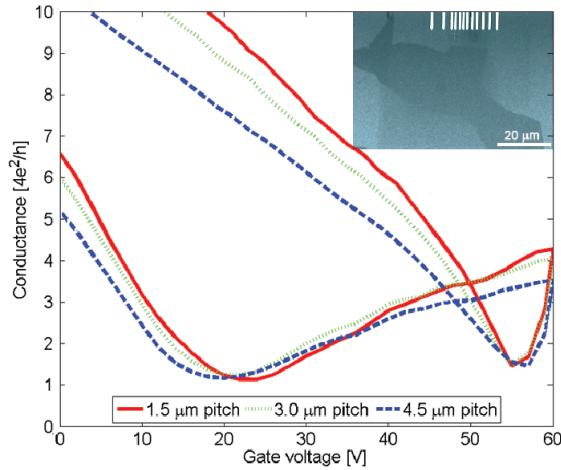


Figure 2. The conductance of a graphene flake in ambient conditions on clean SiO₂ as function of applied gate voltage. The conductance is measured with 10 configurations per gate step and gate voltage steps of 2 V. In each data point, recordings with three different voltage probe pitches, 1.5 μm (red solid), 3.0 μm (green dotted) and 4.5 μm (blue dashed), were done. The insert shows an optical image of a 12-point probe over a single layer of graphene.

for graphene on SiO₂ [4, 5, 27–29]. The effect was explained by Wang *et al* [30] as trapped charges in the SiO₂ leading to a different effective gate voltage experienced by the graphene, as compared to the applied gate voltage. The hysteresis effect is further discussed after vacuum measurements. The carrier mobility was calculated from $\mu = t/\epsilon \times d\sigma/dV_g$ [1], where t is the thickness and ϵ is the permittivity of SiO₂ and V_g is the gate voltage. The mobilities are calculated to be in the range 1000–2500 cm² V⁻¹ s⁻¹.

4. Vacuum conditions

For measurements in a vacuum (10^{-5} Pa), a FEI Quanta 200 ESEM FEG was used. The probes were mounted on a 13-axis SmarAct micromanipulator which was fitted in the ESEM, and all measurements were performed with 1.5 μm pitch probes. After carefully aligning the probe to the plane of the sample, they were brought within 1–2 mm of the surface before evacuating the chamber. Measurement on gold coated regions was used to verify proper operation of the individual electrodes. A DC current of 10 μA was sourced using a Keithley 2400 sourcemeter, while the voltage drop was measured with a National Instrument data acquisition (DAQ) card. The gate voltage was applied by the DAQ card, and amplified using a Falco Systems voltage amplifier. The gate voltage was swept from 0 to +60 to –60 V and back to 0 V in all measurements, at a controllable rate of between 0.4 and 240 V s⁻¹, corresponding to a full sweep frequency between 1.7 mHz and 1 Hz.

Alignment of the M4PP was made with reference to lithographically defined index marks, and the probes were engaged with the graphene sample outside of the field of view of the microscope until electrical contact was measured. This was done in order to avoid exposing the graphene sample to the e-beam irradiation, which has been shown to introduce damage [31–34] as well as contamination on the surface. In order to do fast gate sweeps, we used a single configuration (A) for vacuum measurements. Conductance measurements for three different sweep rates are shown in figures 3(a)–(c), with only the positive gate voltages. For high sweep rates, there is a low signal-to-noise ratio, so multiple sweeps were averaged to produce the data shown.

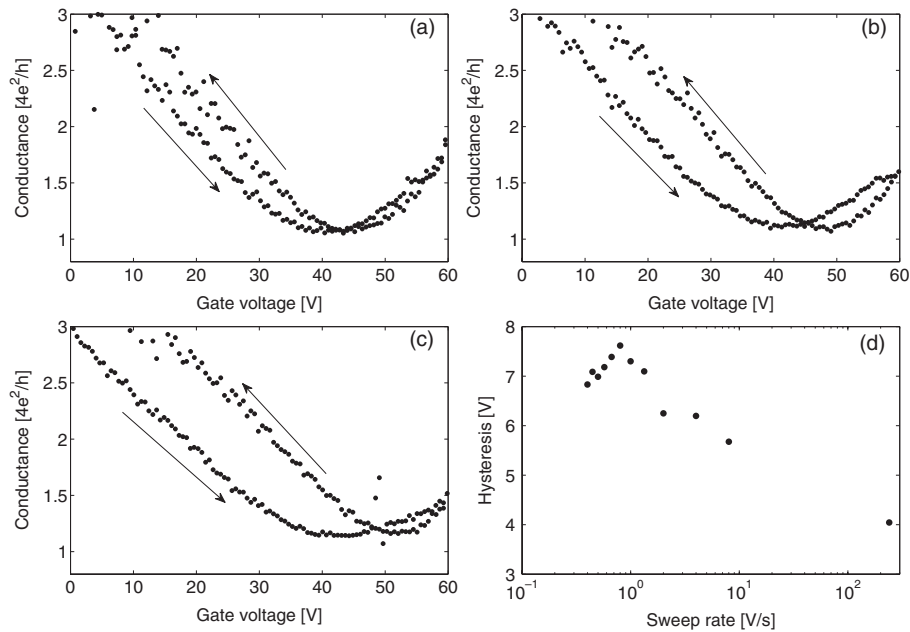


Figure 3. Measurements in a vacuum showing conductance (in $4e^2/h$) as a function of applied gate voltage for different sweep rates: (a) 240 V s⁻¹, (b) 4 V s⁻¹, (c) 0.4 V s⁻¹. Arrows indicate the sweep direction. The hysteresis appears to increase as the sweep rate is decreased. (d) Hysteresis as function of sweep rate, which shows a maximum in hysteresis at 0.8 V s⁻¹. Hysteresis was found by a parabolic fit to the data below a conductance of 1.5 times $4e^2/h$. Error on the fit is negligible.

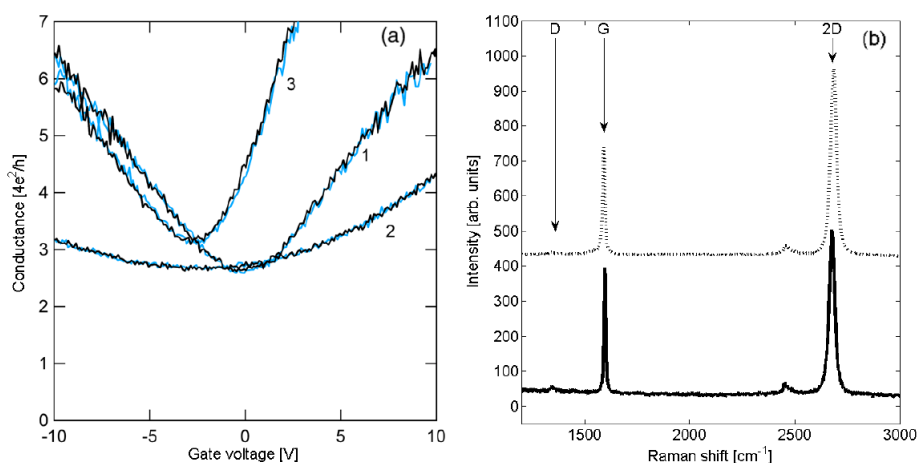


Figure 4. (a) Environmental measurement where the mobility decreases when graphene was exposed to water vapor. Graphene starts in high vacuum (1), water vapor is introduced (low vacuum) (2) and finally high vacuum is achieved again (3). Colors represent up- (black) and down-sweep (blue). (b) Raman spectrum before (solid) and after (dotted) measurements in SEM. The spectrum is shifted for clarity. The ratio of the intensity of the D peak to the G peak remains small after the measurement, indicating that the graphene did not alter in structure using the method described in the text.

The charge neutrality points are calculated by fitting a parabola near the minimum conductance of the up- and down-sweep, and finding the minimum of the fit. The carrier mobility is estimated in the same manner as the measurements in ambient conditions. As the sweep rate is decreased, the hysteresis changes, and the mobilities are observed to decrease slightly from ~ 1200 to $\sim 1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

The variation of hysteresis with sweep time is shown in figure 3(d). It is observed that the hysteresis increases up to 0.8 V s^{-1} , followed by a decrease. This trend was observed on all samples investigated.

In the following work we use an environmental SEM in which a range of gases can be leaked into the sample chamber in order to study the influence of the local gas environment on conductance and mobility. Figure 4(a) shows the effect of water vapor on conductance. First, a high vacuum (10^{-5} Pa) measurement was performed (1), resulting in mobility around $2000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Water vapor was introduced at 400 Pa (2), and the mobility dropped to roughly $500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Evacuating the chamber to 10^{-5} Pa again (3) the mobility was restored to its initial value, with a slight shift in the charge neutrality point and minimum conductivity.

Figure 4(b) shows Raman spectra from pristine graphene samples and graphene samples contacted outside the field of view. The $I(\text{D})/I(\text{G})$ ratio remains small after ESEM measurements, which shows no indication of an increased density of defects [35].

Our results obtained under vacuum in a SEM show that the hysteresis in the charge neutrality point depends on the sweep rate, with a maximum hysteresis at 0.8 V s^{-1} . The hysteresis effect has been observed in many graphene field effect devices, and has been suggested to be caused by charge trapping in the SiO_2 [4, 30].

When changing the gate voltage, the electric field traps or detraps charges at a specific rate. Therefore, it may be expected that the hysteresis will approach zero for high sweep rates since

the traps do not have time to fill. This should lead to a time-dependence of the hysteretic effect, and thus a varying offset of the charge neutrality point. Furthermore, it is expected that a steady state will be achieved for very low sweep rates, so hysteresis should also approach a constant value, possibly zero. Mattmann *et al* [36] demonstrated that pulsing the gate voltage is a highly efficient method to strongly reduce gate hysteresis for carbon nanotube based field effect sensors.

Environmental measurements showed a clear reduction in carrier mobility, when comparing high vacuum to low vacuum with water vapor. These results contradict previous measurements with a variety of adsorbed gases on graphene which showed no change in mobility [37]. We are unable to specifically determine the cause of this contradiction, but suggest that our observations of changing mobility may be due to ionization of water molecules which adsorb onto the graphene surface, and thereby increase the number of charged surface scatterers. Protons and hydroxyl groups may also be able to neutralize some of the charged species already on the surface, which then may desorb from the surface when a high vacuum is reintroduced. This would explain why the mobility is slightly increased when comparing the two high vacuum states.

While we frequently encountered a poor electrical contact to the graphene, damage to the graphene surface was rarely observed. The graphene seemed very resistant to mechanical scratching; however, breakdown occurred consistently at a current of around $100 \mu\text{A}$ or more. This can be explained by a high current density at the contact points, which from previous studies [38] can be expected to be at minimum 100 nm in diameter. Assuming the thickness of the graphene layer to be 3.4 \AA , the current density at the perimeter of a contact area is in rough agreement with the critical current density of graphene of 10^8 A cm^{-2} found experimentally by Murali *et al* [39], at 10^7 A cm^{-2} .

5. Conclusion

We have shown that micro four-point probes can be used to perform local and non-destructive measurements on graphene, within a shorter time span than with commonly used lithographic processing. The sample size is only limited by the electrode pitch, and the non-destructive approach makes further processing of the sample possible. To compete with lithographic contacts, it is of key importance that the approach can be used in a vacuum or controlled atmospheric conditions, which we have demonstrated here. We observed a strong tendency of the carrier mobility to decrease in the presence of water vapor, which conflicts with previous reports. It is anticipated that micro four-point probes could be an invaluable tool for inline verification and process monitoring in graphene fabrication, as well as providing a unique possibility of probing and mapping the local transport properties of graphene.

Acknowledgments

We appreciate financial support by the Danish Research Council for Technology and Production Sciences (Nanoengineered Graphene Devices) as well as helpful discussions with Cosmin Roman and Christofer Hierold, both ETH Zurich, Micro and Nanosystems.

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